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## (54) ANODE MATERIAL FOR NONAQUEOUS ELECTROLYTE SECONDARY BATTERY AND MANUFACTURING METHOD THEREOF

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide an anode material having high capacity and capable of charge and discharge at high rate, and the method thereof.

SOLUTION: The anode material for a nonaqueous electrolyte secondary battery is formed by applying alloy electrolyteless plating on a copper foil as an anode substrate. The directly alloy electrolyteless plating is selected from Sn-Ni, Zn-Ni, and Sn-Co. In the manufacturing method of the anode material, reducing agent for plating is to be a boron hydride compound or a hypophosphite compound so that B or P is included. Furthermore, plating having different compositions in the interior layer and the exterior layer of a copper foil is performed. In the manufacturing method, by heat treatment of the plate coat according to necessity, the plate can be an intermetallic compound.

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CLAIMS

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[Claim(s)]

[Claim 1] The negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by using the copper foil which carried out alloy electroless deposition as a negative-electrode ingredient.

[Claim 2] The negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries according to claim 1 with which alloy electroless deposition was chosen from Sn-nickel, Zn-nickel, and Sn-Co.

[Claim 3] The manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by heat-treating this plating coat and considering as an intermetallic compound after performing alloy electroless deposition to copper foil.

[Claim 4] The manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by making B contain by using a plating reducing agent as a potassium-borohydride compound.

[Claim 5] The manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by making P contain by using a plating reducing agent as a hypophosphorous acid compound.

[Claim 6] The manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by making Cu-Sn and the intermetallic-compound phase of Cu-In generate by heat-treating by covering Sn and In with electroless deposition on copper foil.

[Claim 7] The manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by plating with the presentation in which the inner layer of copper foil differs from an outer layer.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is the thing of a nonaqueous electrolyte rechargeable battery concerning a negative-electrode ingredient and its manufacture approach especially.

[0002]

[Description of the Prior Art] Since it has the description that a nonaqueous electrolyte rechargeable battery is a small light weight, and its energy density is high, while portable-izing of a device and cordless-ization progress, need is increasing rapidly. The lithium content metallic oxide of  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$  grade is known as positive active material, and, as for the conventional nonaqueous electrolyte rechargeable battery, the graphite ingredient which can occlusion emit a metal lithium, and a lithium alloy and a lithium is used as a negative-electrode active material. An intermetallic compound like  $\text{FeSi}_2$  or  $\text{Fe}_{1-(x+y)}\text{Co}_x\text{Ni}_y\text{Si}_2$  as shown in JP,5-159780,A or JP,11-25973,A as a negative-electrode ingredient with a still bigger discharge capacity is proposed. Furthermore, the intermetallic compound with the semimetal and the metal which Si or Sn alloy does not alloy to JP,10-223221,A with Li and the metal to alloy is proposed by JP,9-63651,A.

[0003]

[Problem(s) to be Solved by the Invention] By the conventional approach, the predetermined ingredient which carried out amount weighing capacity was mixed, and it fused at the elevated temperature more than the melting point, it ground after atomization, or the melt spin method or casting, was made a predetermined grain size, and was used as a negative-electrode active material. Moreover, the approach of carrying out and fine-crystal-izing mechanical milling using the ball mill of high energy, as shown in reference (others [ Sakaguchi / electrochemistry p1291 vol66 No12 1998 ]) is proposed. Therefore, the equipment in connection with manufacture was expensive, and it had the problem to which energy cost becomes high. Moreover, since electrical conductivity was small and resistance of the insertion desorption of a lithium also had it, when these intermetallic compounds did not perform well selection or membrane formation of an electric conduction agent or a binder on the occasion of negative-electrode creation, the charge and discharge in a high rate had the problem of being difficult. [ large ] This invention can solve these problems, and can manufacture them with simple equipment by low energy cost, and the intermetallic-compound negative-electrode ingredient which was excellent in the high rate property is offered.

[0004]

[Means for Solving the Problem] In order to solve these problems, the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries of this invention carried out the direct non-electrolyzed alloy plating on the copper foil which is a negative-electrode base material, and became possible [ manufacturing a negative-electrode ingredient according to very little energy and an easy process ]. Therefore, this invention is a negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by using the copper foil which carried out alloy electroless deposition as a negative-electrode ingredient. Moreover, alloy electroless deposition is the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries of said publication chosen from Sn-nickel, Zn-nickel, and Sn-Co. Moreover, after performing alloy electroless deposition to copper foil, it is the manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by heat-treating this plating coat and considering as an intermetallic compound.

[0005] Moreover, it is the manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by making B contain by using a plating reducing agent as a potassium-borohydride compound. Moreover, it is the manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by making P contain by using a plating reducing agent as a hypophosphorous acid compound. Moreover, it is the manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by making Cu-Sn and the intermetallic-compound phase of Cu-In generate by heat-treating by covering Sn and In with electroless deposition on copper foil. Moreover, it is the manufacture approach of the negative-electrode ingredient for nonaqueous electrolyte rechargeable batteries characterized by plating with the presentation in which the inner layer of copper foil differs from an outer layer.

[0006] In this invention, alloy plating is possible, and manufacture of the negative-electrode ingredient in which the charge and discharge in a high rate are possible is possible at high capacity by applying a lithium, Sn, Zn and In to alloy, a lithium, and nickel which is not alloyed and the alloy by the combination of Co. Considering as an intermetallic compound is also possible by furthermore heat-treating a plating coat if needed.

[0007]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The negative electrode of high capacity was obtained by using the alloy which consists of at least one sort one sort of Sn, Zn, and In, and in nickel and Co as mentioned above in this invention on copper foil as a negative-electrode active material created with direct nonelectrolytic plating. Although Zn, Cd, aluminum, Ga, In, Si, germanium, Sn, Pb, As, Sb, Bi, etc. are raised as a lithium and a metal alloyed easily, if it takes into consideration that nonelectrolytic plating is possible, not causing a pollution problem in the case of abandonment, etc. from a water solution, Sn, Zn, In, etc. will be chosen.

[0008] Although Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Zr, Nb, Mo, Ta, W, noble metals, etc. are raised as a lithium, the metal which is not alloyed, and a semimetal element, nickel and Co are chosen as a common element in which Above Sn etc. and alloy electroless deposition are possible. Since Sn and nickel deposit in the condition of having been mixed with homogeneity, these non-electrolyzed alloy-plating

coats do not have the need of taking the melt spin method which is stated to JP,11-25973,A or JP,10-223221,A, and a complicated process like mechanical alloy INGU, and carrying out detailed-ization of a crystal. Moreover, it becomes possible to control the crystal particle diameter and deposit gestalt which deposit by examining plating conditions, such as an additive, whenever [ bath presentation or bath temperature ].

[0009] The thing of the presentation which is in the usual reference as a non-electrolyzed alloy plating bath is usable. Generally, in Sn alloy system and Zn alloy system, an alkaline bath is usable. When an electroless deposition coat is used, it is possible by introducing P and B so much into an alloy coat to make a crystal lattice distorted and to make \*\*\*\*\* of a lithium easier. Although the copper foil of a base material is not usually used for a nonaqueous electrolyte rechargeable battery and is satisfactory, rolling copper foil and electrolytic copper foil are usable. The thickness needs to hold the constitutionally required thickness and the reinforcement of a cell. By rolling copper foil, it is 18 micrometers from 12 micrometers in thickness, and the low foil of 18-micrometer surface roughness is used from 9 micrometers in thickness with electrolytic copper foil.

[0010] Since the thickness of plating is regulated by the thickness of the coat which can carry out electroless deposition although the thickness which can secure the capacity demanded as a negative electrode is needed, the not much thick thing is industrially difficult. Usually, it is used by 2 to about 50 micrometers. When it furthermore heat-treats and considers as an intermetallic compound, in the case of the not much thick coat, it has the problem to which a coat becomes remarkably hard for the intermetallic compound containing P or B, and revolution rolling up becomes difficult in the case of cell creation. Therefore, it is preferably used by 5 to 20 micrometers.

[0011] About heat-treatment, since a plating coat has the already thin shape of 30-micrometer order and film, intermetallic-compound-ization is attained very much with heating in a short time. Moreover, since alloying advances in the copper foil of a base material when it processes at an elevated temperature too much, it is not desirable. When electroless deposition of the single metal is carried out, it is possible to carry out alloying with the copper foil of a base material with heating. The electric furnace by which ambient atmosphere control was carried out is common so that it may not oxidize as a heat treatment equipment, but a processing object is a nonelectrolytic plating coat, and since heat capacity is small, it is also possible to heat a plating foil continuously using a reflective type heating furnace like a gold furnace.

[0012] It is possible to change the coat presentation of the interior and the exterior continuously by plating continuously using the plating bath from which plating conditions are changed in the start of plating and an end in the case of electroless deposition, and a bath presentation [ \*\*\*\* / changing the presentation of a deposit coat ] differs. Such a coat is usually called an inclination presentation coat. For example, by the nickel-Sn system, the interior is considered as the presentation of an intermetallic compound of nickel<sub>3</sub>Sn<sub>4</sub>, and the exterior becomes possible [ suppressing the effect of change of the grid by \*\*\*\*\* of Li by considering as an alloy with few Sn contents like nickel<sub>3</sub>Sn ].

[0013] Furthermore, it is also possible to use the plating bath presentation of a inner layer and an outer layer as a multilayer coat by completely changing. For example, electroless deposition of the nickel-Sn coat as a cathode active material is carried out to the interior, and it also becomes possible by carrying out high grade electroless nickel plating thinly by porous one into an outer layer part to prevent exfoliation of the plating coat accompanying \*\*\*\*\* of a lithium.

[0014]

[Example] 50ml sodium hypophosphite 10 g/L of example 1 nickel-sulfate 35 g/L chlorination 2nd tin 35 g/L sodium-citrate 85 g/L ammonium-chloride 50 g/L 28% aqueous ammonia was dissolved in water, and the nickel-Sn-P radio solution alloy plating bath was created. Electrolytic copper foil was immersed in the electroless deposition bath which agitated weakly after the chlorination tin-palladium solution immersion which is the usual catalyst-ized processing, and carried out plating for 20 minutes in 90 degrees C. What contained the plating coat nickel<sub>45</sub>%Sn<sub>52</sub>%P<sub>3</sub>% by 20 micrometers of thickness was obtained. When epithelial tissue was identified according to the X diffraction, the peak of nickel, nickel-P, and Sn was checked. The cell property sandwiched the commercial separator (the product made from polypropylene 25 micrometers) using 2 pole type model cel between the trial poles which made the 0.2mm metal lithium the counter electrode, and clipped it disc-like, and evaluated it to the electrolytic solution using one-mol LiBF<sub>4</sub>/PC+EMC. The potential scan was carried out between 0.05V-1.2V pair Li(s). An evaluation result is shown in Table 1.

[0015]

[Table 1]

実施例	皮膜組成 (wt%)	熱処理	容量密度 (mAh/g)	容量密度 (mAh/cm <sup>2</sup> )
1	45Ni-52Sn-3P	なし	180	1200
2	61Ni-35Zn-4P	なし	125	900
3	43Co-54Sn-3P	なし	185	1370
4	45Ni-52Sn-3P	有り	195	1370
5	47Ni-52Sn-1B	なし	184	1330
6	100In	有り	150	1080
7	45Ni-52Sn-3P/Ni	なし	170	1190

[0016] Example 2 nickel-chloride 35 g/L zinc chloride 7 g/L sodium-citrate 118 g/L sodium hypophosphite 64 g/L was dissolved in water, and aqueous ammonia adjusted pH to 10. It was immersed in the plating bath agitated weakly after carrying out the usual catalyst-ized processing to electrolytic copper foil, and plating was carried out for 20 minutes in 65 degrees C. The object which contained the plating coat 35% [ of nickel 61% zinc ] P 4% by 15 micrometers of thickness was obtained. When coat tissue was identified according to the X diffraction, the peak of nickel, nickel-P and Zn was checked. Cell characterization was performed like the example 1.

[0017] Using the cobalt chloride instead of the nickel chloride of example 3 example 1, the initial make-up of electrolytic bath of the electrolytic bath was carried out, and the rest galvanized it like the example 1. The object which contained the plating coat Co43%Sn54% P3% by 22 micrometers of thickness was obtained. When the coat presentation was identified according to the X diffraction, the peak of Co, Co-P, and Sn was checked. Cell evaluation was performed like the example 1.

[0018] 600 degrees C of coats which deposited in the example 4 example 1 were heated for 5 minutes in the argon ambient atmosphere. When the plating coat after heating was identified according to the X diffraction, it had become nickel-P and the mixture of the intermetallic compound of nickel3Sn4. Cell evaluation was carried out like the example 1.

[0019] an example -- 2nd tin of 35 g/L chlorination 35 g/L potassium-sodium-tartrate 60 g/L sodium-borohydride 2.3 g/L was dissolved in water 5 nickel chloride, it adjusted to pH12.5 by NaOH, and the nickel-Sn-B electroless deposition bath was created. It was immersed in the plating bath which agitated electrolytic copper foil weakly after the usual catalyst-ized processing for 10 minutes at 40 degrees C. The object which contained the plating coat nickel47%Sn52%B1% by 15 micrometers of thickness was obtained. When epithelial tissue was identified according to the X diffraction, the peak of nickel, nickel-B, and Sn was checked. Cell evaluation was carried out like the example 1.

[0020] Example 6 indium-sulfate 5 g/LEDTA and 2Na7 g/L triethanolamine 3 g/L sodium-borohydride 2 g/L was dissolved in water, and the non-electrolyzed indium bath was created. It was immersed in the plating bath which agitated electrolytic copper foil weakly and maintained it at 80 degrees C by pH9.5 after the usual catalyst-ized processing for 10 minutes. The plating coat was 20 micrometers of thickness. Heat treatment was carried out for 3 minutes at 450 degrees C under the argon ambient atmosphere. When the coat presentation was identified according to the X diffraction, eta phase and delta phase have been checked. Cell evaluation was carried out like the example 1.

[0021] It galvanized for 3 minutes at 65 degrees C using the usual electroless-nickel-plating bath marketed from the coat galvanized like example 7 example 1. The plating coat had become the two-layer structure where 2 micrometers of nickel-P coats were plated, on the

nickel-Sn-P coat. Cell evaluation was carried out like the example 1.

[0022]

[Effect of the Invention] In this invention, a negative-electrode ingredient with big \*\* capacity consistency can be easily manufactured with a non-electrolytic decomposition process.

\*\* Since copper foil is made electrodeposited directly without using it, the conductivity of an electric conduction agent etc. is good.

\*\* Since it is uniting with copper foil, it deals with and is easy.

\*\* It is possible to make expansion contraction of the crystal accompanying the insertion desorption of a lithium ease by B, P, etc. being incorporated in a coat so much.

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